



PROCESS FOR GENERATION OF PRECIPITATED CALCIUM
CARBONATE FROM CALCIUM CARBONATE
RICH INDUSTRIAL BY-PRODUCT

5 **Field of the Invention**

The present invention relates to a process for the production of precipitated calcium carbonate from a calcium carbonate-carbonate-rich by-product generated in an industrial processes, specifically, a by-product in-generated by a nitrophosphate plants in the fertilizer industry.

RECEIVED

NOV. 12 2003

TC 1700

10

Background of the Invention

~~Precipitated calcium carbonate is produced by calcination of calcium carbonate rich by product into quick lime in a kiln, followed by slaking or hydration to obtain hydrated lime and subsequently subjecting it to carbonation.~~

15

Precipitated calcium carbonate finds varied commercial uses ~~like, in,~~ including the manufacture of paper, rubber, plastics, glass, textiles, putties, chalks, sealant, adhesives, paints, inks, varnishes, food, cosmetics, dentrifices, chemicals and pharmaceuticals.

20

Commercial applications of precipitated calcium carbonate require well-defined powder characteristics, particularly, fine particles with a narrow size distribution, uniform shape and crystallinity. Marentette J.M. *et al.* ("~~Crystallisation~~Crystallization of Calcium Carbonate in the presence of PEO-block-PMAA copolymers", *Adv. Mater.*, 9, 647, 1997) have shown that these characteristics play a crucial role in product properties and that their control is important for the preparation of industrially useful products. ~~The p~~Precipitated calcium carbonate must also ~~needs to~~ be substantially free of impurities ~~for being to~~ be useful for various commercial applications. Several physical and chemical processes have been reported for the treatment of solid waste containing calcium carbonate.

30

Physical processes requires drying and grinding to ~~such~~ a fineness that allows impurities ~~can to~~ be removed by screening, classification, magnetic separation, hydrocyclone and floatation separation. The disadvantages of these physical methods ~~are~~ include the requirement of special

~~machines/devices/equipment and its the required maintenance thereof.~~ Other disadvantages of existing processes include ~~The unpredictable process efficiencies, variation-variable in results of in the quantities of impurities removed and the expenses associated with employing such physical techniques—are other~~
5 ~~disadvantages.~~

Chemical processes for the purification of calcium carbonate-rich waste involves leaching or bleaching of impurities using special reagents. Disadvantages of these methods ~~are that it include the require-requirement of a number of unit operations to perform the treatment.~~ Moreover, a single chemical process may not
10 ~~be suitable to-for remove-removal of~~ all the impurities. Removal and separation of excess chemical reagents after the treatment is another disadvantage.

Another previously known and widely used method for the treatment of calcium carbonate-rich waste is reburning within the kiln and removing ~~it-the~~ reburned waste after cooling ~~so-as~~ to obtain calcium oxide. The calcium oxide
15 ~~which is then~~ recycled in a causticizing process in producing paper pulp or it is subjected to hydration followed by carbonation to produce precipitated calcium carbonate.

~~Reference may be made to US patent No. 4,018,877 (1977) to Richard Derek Anthony Woode according to which~~ In the process of Richard Woode (US
20 Patent 4,018,877), an aqueous suspension of calcium hydroxide at 25° C ~~is-was~~ agitated vigorously and reacted with a mixture of air and carbon dioxide. After 15 minutes (following the 'primary nucleation stage') a complex-forming agent ~~for calcium ions,~~ such as a hydroxy carboxylic acid, especially-particularly a hydroxy poly-carboxylic acids (for example, e.g., Citric-citric acid and malic acid) which
25 complexes calcium ions. The complexing agent was added in ~~at~~ the concentration range of 0.001 to 5 wt.%, ~~especially-preferably~~ in the range 0.03 to 0.2 wt.% ~~by weight based on the weight of the calcium carbonate produced, is-added.~~ The carbonation was stopped after about-a further 50 minutes when the reaction mixture had just become acid to a phenolphthalein indicator. The mixture ~~is-was~~ then
30 heated to 85° C over a period of 20 minutes and ~~is-was~~ allowed to age for 30 minutes. Carbonation ~~is-was~~ restarted at ~~the-a~~ much lower rate, maintaining the temperature ~~to-at~~ 85° C, ~~and-a~~ After 20 to 40 minutes the pH of the batch had fallen

below 8.0. At this stage, 0.8% of stearic acid in ammoniacal solution ~~is was~~ added and the mixture ~~is was~~ stirred at 85°C for about 3 hours. The suspension ~~is was~~ filtered, ~~and The~~ filter cake ~~is was~~ extruded through 5/16 inch diameter holes to yield "granules" which ~~are were~~ dried in an oven overnight at 130°C on a gauze-tray to produce calcium carbonate having 0.72 relative granule hardness and 0.07 micron ultimate particle size with a soft texture. The drawbacks of this process are that the total batch/production time is more than 5 hours during which time the temperature is maintained at 85°C for a period of 4 hours. ~~and In addition, the process requires~~ drying of the product overnight at 130°C ~~for overnight period~~.
10 This ~~makes this process~~ is thus highly energy consuming and is therefore unattractive.

~~In US Patent No. 4,133,894 (1979) to Hiroji Shibasaki et al. (US Patent 4,133,894), it is disclosed~~ disclose that the precipitates of uniform particle size can be continuously produced by repeating the step of carbonation reaction. In the first
15 step of the process, a suspension of calcium hydroxide having a solids concentration 0.1 to 10 weight % and a temperature of 15 to 30°C is sprayed in the form of droplets of about 0.2 to 1.0 mm in diameter against a gas containing 10 to 40 volume % carbon dioxide in countercurrent contact therewith; ~~the The~~ gas ~~being is~~ passed at a specified superficial velocity of about 0.02 to 0.5 m/sec;
20 ~~whereby~~ By this process, 5 to 15% of the calcium hydroxide is converted to calcium carbonate. In the second step of this process, the suspension resulting from the first step is sprayed in the form of droplets of about 1.0 to 1.5 mm diameter against a gas containing 15 to 35 volume % of carbon dioxide and passed upward through the column at a superficial velocity of about 1.5 to 2.5 m/sec
25 whereby growth of ~~the~~ crystals is accomplished. In the third step of this process, the suspension resulting from second step is sprayed at a temperature of up to 30°C ~~and~~ in the form of droplets of about 1.5 to 2.0 mm in diameter into a column in countercurrent contact at a superficial velocity of about 1.5 to 3.0 m/sec; whereby the carbonation is completed. Thus, superfine calcium carbonate having an
30 average particle size of less than about 0.1 to 3.0 microns is produced. The main drawback of this ~~invention process~~ is that it ~~needs requires~~ control of number of parameters such as solids concentration, droplet size, temperature of suspension,

gas velocity of carbon dioxide containing gas etc. ~~at a time~~ for three columns. Another drawback is use the requirement of multi-step carbonation which is more expensive in terms of operating cost for columns and pumps than a require much capital investment for columns and pumps and the operating cost, compared to
5 single stage carbonation.

US patent ~~5,342,600 (1994) issued to Bleakley, Ian S. et al. (US Patent 5,342,600)~~ describes a method of preparing precipitated calcium carbonate which comprises: (1) slaking quick lime in an aqueous medium, (2) subjecting the said aqueous medium to continuous agitation during said slaking, (3) passing a
10 suspension of calcium hydroxide obtained after slaking through a sieve having an aperture size of 40-70 microns, (4) subjecting the suspension to high energy high shear agitation with an impeller having a peripheral speed of 40-70 m/sec., so as to obtain finely dispersed calcium hydroxide, (5) terminating the said high energy high shear agitation on achieving finely dispersed slaked lime, (6) carbonating this
15 suspension the finely dispersed slaked lime by passing therethrough sufficient gas comprising carbon dioxide to eause the neutralize the pH of the suspension to fall to neutral, during said carbonation step, (7) subjecting the said suspension to continuous agitation to maintain the suspension with an impeller speed of 200-700 cm/sec to maintain the suspension, and separating (8) separating the precipitated
20 calcium carbonate formed in the process. The disadvantage associated with this method is requirement of for generating high energy high shear agitation during slaking and carbonation.

The use of additives to control the morphology and particle size is recommended also reported. ~~As per the US patent No. 5,558,850 (1996) to~~
25 ~~Bleakley Ian S. et al. (US patent 5,558,850) disclose, a process wherein 0.1 to 2.0% by weight of a reagent having one or more active hydrogen atoms e.g., polyhydric alcohol or phenol is added to the aqueous medium in which the quick lime is slaked. As per the US patent No. 5,332,564 (1994) to Chapnerkar Vasant D. et al. (US patent 5,332,564) disclose a process wherein, quicklime is slaked in an~~
30 aqueous solution containing about 0.1 to 2.0% by weight of a sugar for the production of rhombic shaped precipitated calcium carbonate, and as per the US patent No. 5,232,678 (1993) to Bleakley Ian S. et al. (US Patent 5,232,678),

disclose a process wherein 0.01 to 1.5-% by weight of triethanolamine, mannitol, morpholine and solid boroheptonate are employed infor the preparation of clusters of calcium carbonate which give good light scattering properties when used as a paper filler or paper coating pigment. ~~The US patent No. 4,714,603 (1987) to~~
5 ~~Vanderheiden, Denis B. (US patent 4,714,603) mention-discloses~~ the use of polyphosphates in an amount of 0.1 to 1.0 % by weight for ~~getting-generating~~ precipitated calcite of substantially spherical morphology suitable for use in dull finish coated paper. The disadvantage associated with all these processes is the requirement of special reagents which adds to the production cost.

10 ~~US Patent No. 5,833,747 (1998) to Bleakley Ian S. et al. (US Patent 5,833,747),~~ discloses a method for preparing precipitated calcium carbonate for use as a pigment in paper coating compositions. The method ~~comprising-compriscs~~ the steps of (1) carbonating an aqueous medium containing lime, (2) at least partially dewatering the precipitated calcium carbonate-containing suspension using a
15 pressure filter device operating at a pressure of 5 to 10 MPa- and (3) subjecting the precipitated calcium carbonate-containing suspension to comminution by high shear attrition grinding with an attrition grinding medium such as silica sand having a median particle diameter in the range 0.1 to 4.0 mm. The product predominantly comprises aragonitic or scalenohedral crystals. The disadvantages
20 of this method ~~are that it required~~include the requirement of a device for high shear attrition grinding with a special grinding medium ~~which is not separated during the process~~ and a pressure filter device for dewatering the precipitated calcium carbonate containing suspension. Also, the grinding medium is not separated during the process.

25 ~~The process as described in US Patent No. 5,695,733 (1997) to Kroc Vicki J. et al.,~~ disclose a process (US patent 5,695,733) that comprises the steps of (1) forming a reaction mixture containing seed material of a scalenohedral particles of aragonite type calcium carbonate and (2) adding lime slurry into the reaction mixture while simultaneously introducing carbon dioxide. The flow rates of the
30 lime slurry and carbon dioxide are adjusted to control the solution conductivity of the reaction mixture to ~~between-from~~ 2 to 4 milli Siemens to form the clusters of calcite particles. The drawbacks of this process is that it requires simultaneous

addition of lime slurry and carbon dioxide ~~for to~~ maintaining the solution conductivity. Moreover, simultaneous control of flow rates of both liquid phase and gaseous phase reactants simultaneously are ~~is~~ difficult to administer.

You Kyu Jae discloses A a process for producing calcium carbonate
5 particles having an average size of 0.1 to 1.0 micron is described in (US patent
No.5,811,070 (1998) to You Kyu Jae. The process comprising comprises the
following steps of: (1) introducing eCarbon dioxide is introduced into a milk of
lime containing a first reagent, such as consisting of sodium glutamate, sugar, and
or a mixture thereof, in the range of 0.1 to 2.0 parts per 100 parts of calcium
10 hydroxide initially present in the milk of lime, to prepare an aqueous suspension
containing calcium carbonate particles of 0.4 micron in average size. The
concentration of the first reagent is from 0.1 to 2.0 parts per 100 parts of calcium
hydroxide initially present in the milk of lime.; (2) adding aA milk of lime is
added into the above aqueous suspension. (3); and continuously reacting aA
15 carbonated solution is added to the aqueous suspension, which containing contains
a second reagent including comprising at least one of sodium polyacrylate and a
bicarbonate in the range of 0.1 to 5.0 parts per 100 parts of calcium hydroxide
present initially, with the aqueous suspension. Calcium carbonate particles
according to produced by the process are suitable as a filler for adhesives, paints,
20 inks, papers and plastics, especially Polyethylene-transparent polyethylene films.
The drawbacks associated with this process is the addition of two different types of
reagents in two stages, both of which are of different types, which. This makes the
process complicated and unattractive.

US Patent No.4,367,207(1983) to Vanderheiden-Dennis B discloses a
25 process (US Patent 4,367,207)., concerned with a process for preparing finely
divided precipitated calcite. In the Vanderheiden process, in which carbon dioxide
is introduced into an aqueous calcium hydroxide slurry containing anionic organo-
polyphosphate polyelectrolyte with the carbonation started at a temperature above
from about 7°C and below to about 18°C. The drawbackOne disadvantage of this
30 process is that it requires the requirement of an anionic polyelectrolyte which adds
to the production cost. Another disadvantage is maintaining the required
maintenance of a reaction temperature below ambient temperature. This

requirement necessitates, which require a chilling plant and it is which is energy consuming.

Summary of the Invention

5 The present invention provides a process for the production of precipitated calcium carbonate from calcium carbonate--rich by-product generated in a chemical processing industry which process obviates the drawbacks as--detailed above. Precipitated calcium carbonate is produced by calcination of calcium carbonate-rich by-product into quick lime in a kiln. This is followed by slaking or hydration
10 to obtain hydrated lime. The hydrated lime is subsequently subjected to carbonation.

 The present invention also develops an alternative ~~source~~ to limestone as a source for producing precipitated calcium carbonate useful for commercial applications.

15 The present invention also develops a process for purification, calcination, slaking and carbonation of a calcium carbonate--rich by-product having particle size in the range of from 20 to 150 microns to produce precipitated calcium carbonate of particle size less than 20 microns.

 The present invention also provides a continuous process for the
20 purification of a calcium carbonate rich by-product from--of a nitrophosphate fertilizer plant in order to thereby minimize--minimizing solid waste produced by such a plant.

 The present invention also provides pollution abatement measures ~~in--for a~~
25 nitrophosphate fertilizer plant by utilization--utilizing of the calcium carbonate--rich by-product generated in such a plant.

 The present invention also produces ~~high value finely divided precipitated calcium carbonate useful as filler in paints, plastics, rubber, poly vinyl chloride (PVC) and paper~~ from calcium carbonate rich by-product generated in a
30 nitrophosphate fertilizer plant, a high-value finely divided precipitated calcium carbonate which is useful as a filler in paints, and in plastics, rubber, poly vinyl chloride (PVC) and paper.

The present invention relates to a process for the production of precipitated calcium carbonate from calcium carbonate-rich by-product generated in industrial processes, specifically from a nitrophosphate plant of in the fertilizer industry. In one embodiment, the steps of the process is comprising:

- 5 — (1) ~~calcination~~ calcinating of a calcium carbonate rich by-product generated in a nitrophosphate fertilizer plant, the by-product having a moisture content up to 25% and a particle size ~~in the range from~~ 20 to 150 microns, in a rotary calciner at a continuous feed rate ~~of from~~ 5 to 20 kg/h at ~~the a~~ calcination temperature of above 850° C and below about 950° C with
10 ~~the a~~ residence time ~~of from~~ 60 to 90 minutes, so as to obtain a calcined material having from 75 to 88% available calcium oxide;
- (2) removing water vapors, volatile matters, ammonia, NO_x and carbon dioxide during the calcination using a blower and a scrubber;
- (3) slaking the calcined material (calcium oxide) in a slaker provided
15 with an agitator rotating at 120 RPM to produce a hydrated lime slurry having a solids concentration in the range from 15 to 23% by weight;
- (4) removing heavier and coarse particles from the hydrated lime slurry by wet sieving through a 60 to 100 mesh sieve to form a fine hydrated lime slurry;
- 20 — (5) diluting the fine hydrated lime slurry to a desired solids concentration ~~in the range from~~ 10 to 20% by weight;
- (6) ~~taking~~ transferring the diluted lime slurry to a carbonation tower and passing a carbon dioxide-air mixture containing 25 % by volume carbon dioxide at a superficial gas velocity of from 10 to 15 cm/sec. ~~maintaining the~~
25 at a maintained temperature in the range from 25 to 45° C until the pH of the diluted lime slurry ~~fallen to~~ is lowered to near neutral;
- (7) separating the precipitates formed in step (6) by known methods, e.g., filtration or centrifugation;
- (8) drying and pulverizing the ~~solids~~ separated precipitates to get
30 produce a precipitated calcium carbonate; and
- (9) optionally, treating the product slurry before ~~filtration~~ the separation with a fatty acid ~~or its salt~~ or a salt of a fatty acid such as, for example,

stearic acid or sodium stearate, at 95° C in ~~the~~ a concentration range of ~~from~~
2 to 3.5% so as to obtain a coated precipitated calcium carbonate which is
industrially useful in a number of applications such as rubber, plastics, paints
and PVC.

5

The invention is further directed to a precipitated calcium carbonate product
having a mean particle size of from about 4 to 6 microns and ~~wherein~~ 100% of the
particles are less than 20 microns and having a weight percent of calcium carbonate
greater than 97.

10

The process described herein significantly purifies a calcium carbonate-
rich by-product generated in a nitrophosphate fertilizer plant to ~~get~~ produce
precipitated calcium carbonate.

Brief Description of the Figures

15

Figure 1 ~~accompanying this specification represents the machines/ equipments of~~
~~the unit apparatus~~ used for the calcination and production of precipitated calcium
carbonate from a calcium carbonate ~~carbonate-rich~~ by-product generated in a
nitrophosphate fertilizer plant.

20

The ~~unit apparatus~~ embodies comprises the following ~~equipments~~ components:

M-paddle mixer cum screw feeder,

S₁-Indirect rotary dryer,

S₂-Indirect rotary calciner,

25

S₃- Jacketed Cooler,

P₁- Jaw crusher,

T₁-Slurry tank;

T₂ -lime slaker,

T₃ - sedimentation tank,

30

C- Carbonation tower with sparger,

F- ~~Filtration~~ Filtration unit, pressure or rotary vacuum type and

D-Flash dryer.

The numbers 1 to 9 in Fig. 1 indicate the following:

1. Calcium carbonate rich by-product, *i.e.*, Feed material.
2. Water
3. Coating agent solution
- 5 4. Steam
5. Filtrate
6. Product
7. Flue gases
8. Exhaust gases
- 10 9. Grit / sediments.

Detailed Description of the Invention

Accordingly, ~~the~~ The present invention provides a process for the production of precipitated calcium carbonate from calcium carbonate-rich by-product generated in industrial processes, specifically from nitrophosphate fertilizer plants. The process of the invention ~~which comprises feeding continuously the a wet calcium carbonate-carbonate-rich by-product containing up to 25% moisture and having particle size in the range of from 20 to 150 microns, continuously into a calciner. The calciner is maintained in the at a temperature range from 850° to~~ 15 950°C. The calciner is operated ~~, with an angle of inclination of 1.08 degrees and a shell rotation speed of from 0.5 to 2 RPM. The calcium carbonate-rich by-product is added to the calciner, at a feed rate of from 5 to 20 kg/h, and The calciner is further provided with the arrangements means to remove the liberated water vapors, carbon dioxide, ammonia and NO_x-containing exhaust gas into a scrubber wherein ammonia and NO_x gases are scrubbed with water. The calciner is further provided with a means to, taking move the calcined outlet material coming out~~ 20 exiting the calciner after residence time of about 30 to 90 minutes, and exiting the calciner at the outlet rate of 2.5 to 6 kg/h, to a crusher (e.g. a Jaw crusher). The crusher crushing-crushes the calcined material using a suitable crusher (e.g. Jaw 25 crusher) to form small lumps. The crushed calcined material is, cooling-cooled it into the a temperature range of from 40 to 50°C, slaking-and slaked with water in a slaker which is provided with an agitator, to produce a hydrated lime slurry having 30

a concentration from 15 to 23% solids by weight. The hydrated lime slurry is processed, followed by removing heavier and coarser particles by sedimentation and / or wet sieving through a 60 to 100 mesh sieve. The processed hydrated lime slurry, diluting the slurry is then diluted to a desired concentration in the range from 10 to 20% solids by weight. The diluted slurry is then taken, taking it up in a carbonation reactor and passing a carbon dioxide-air mixture is passed through the slurry. The carbon dioxide-air mixture containing contains 25% by vol. carbon dioxide and is passed through the slurry at the a gas velocity in the range from 10 to 15 cm/sec., maintaining the at a maintained temperature in the range offrom 25 to 45° C. The carbon dioxide-air mixture is passed through the slurry, until the pH of the slurry has fallen to near neutral. Material that precipitates during the carbonation is then , separating separated the precipitated material formed by known methods, e.g. by filtration or centrifugation drying. The separated material is dried and pulverizing pulverized the solid to get produce precipitated calcium carbonate, optionally Optionally, treating the slurry is treated before filtration with a fatty acid derivative such as sodium stearate at 95°C in the a concentration range from 2.0 to 3.5% by weight for 10 minutes at 95°C. and allowing The treated slurry is then allowed to cool to below 50°C with continuous stirring to get produce coated calcium carbonate. The slurry of coated calcium carbonate thus produced is then separated followed by separation of the solid using known methods, The separated material is then drying dried and pulverizing pulverized the solid to get produce coated calcium carbonate.

In an one embodiment of the present invention, calcium carbonate-rich by-product having a moisture content up to 25% may be used as a starting material. This provides the special advantage of using calcium carbonate-rich by-product as it is generated in the nitrophosphate fertilizer plant or as it is stored for a longer period in silos. Therefore, the process provided by the present invention can be linked to the nitrophosphate fertilizer plant. The process of the invention may thereby be made continuous with the production of calcium carbonate-rich by-product by the nitrophosphate fertilizer plant. and made continuous.

In another embodiment of the present invention, a calcium carbonate carbonate-rich by-product of a nitrophosphate fertilizer plant can be utilized on a

continuous basis to obtain quick lime, slaked lime and/or subsequently precipitated calcium carbonate for commercial applications.

In yet another embodiment of the present invention, the whiteness brightness, lightness, fineness, oil absorption, alkalinity and purity are improved by
5 the present invention.

In yet another embodiment of the present invention, moisture up to 25%, volatile matters from 7 to 8% and ammonium compounds from 0.1 to 0.3% (as ammonical Nitrogen) present in a calcium carbonate-carbonate-rich by-product is are removed.

10 In yet another embodiment of the present invention, nitrate impurities in the range from 0.05 to 0.1% (as nitrate Nitrogen) ~~is~~are removed from ~~the~~a calcium carbonate-carbonate-rich by-product generated in a fertilizer plant.

In yet another embodiment of the present invention, the material outlet rate from the calciner may be adjusted ~~to~~in a range from 2 to 6 kg/h by varying the
15 rotation speed of the calciner from 0.5 to 2 RPM at the angle of inclination of 1.08°.

In yet another embodiment of the present invention, the calcination of calcium carbonate-carbonate-rich by-product may be carried out at ~~the~~a temperature above 850°C and below 950°C to obtain a calcined material having
20 from 75 to 88 % available CaO.

In yet another embodiment of the present invention, the cooled and crushed calcined material may be slaked in water to obtain a hydrated lime slurry having from 15 to 23% solids in suspension.

In yet another embodiment of the present invention, the hydrated lime
25 slurry may be diluted to a desired concentration in the range from 10 to 20% by weight solids and then wet sieved through a 60 to 100 mesh sieve to remove grit particles.

In yet another embodiment of the present invention, the hydrated lime slurry is subjected to carbonation in a bubble column reactor equipped with a
30 suitable sparger and using a carbon dioxide-air mixture having a carbon dioxide concentration of 25% by volume.

In yet another embodiment of the present invention, the carbonation may be accomplished by passing the mixed gas at ~~the~~ a rate of from 10 to 15 cm/sec and maintaining the temperature in the range from 25 to 45° C to achieve ~~the~~ a neutral pH within from about 60 to 140 minutes.

5 In yet another embodiment of the present invention, the precipitated calcium carbonate formed in the process may be coated with a fatty acid derivatives to obtain from 2 to 3% total fatty matter ~~acid derivative~~ in the final product.

10 In yet another embodiment of the present invention, the purity of the calcium ~~earbonate~~ ~~carbonate~~-rich by-product is improved from 88-90% to 97-99% by producing the precipitated calcium carbonate.

Calcium ~~earbonate~~ ~~carbonate~~-rich by-product generated in industrial processes, specifically in a nitrophosphate fertilizer plant, ~~is~~ ~~may~~ containing comprise from 88- to 90% CaCO₃, from 0.2 to 0.4% total nitrogen ~~0.2-0.4%~~, from 15 0.1 to 0.3% ammonical nitrogen ~~0.1-0.3 %~~, from 0.05 to 0.1% nitrate nitrogen ~~0.05-0.1%~~, from 1.0 to 1.5% phosphate as P₂O₅ ~~1.0-1.5%~~, from 0.2 to 0.25% Fluoride ~~fluoride~~ as F⁻ ~~0.2-0.25%~~, from 3.5 to 4.0% mixed oxides (aluminum, iron, phosphates and matter insoluble in HCl) ~~3.5-4.0%~~, from 7 to 8% volatile matter ~~7-8%~~, from 43 to 45% loss on ignition ~~43-45%~~, from 0.1 to 0.15% soluble alkali as 20 Na₂O ~~0.1-0.15~~ and from 1.0 to 1.2% acid insoluble matter ~~1.0-1.2%~~. Moreover Other properties of the by-product include the following, ~~the~~ ~~The~~ pH of a 5% aqueous suspension is from 9- to 9.3, the tapped bulk density is from 1.30- to 1.35 g/ml in L, the brightness/whiteness is 85% and the particle size ~~in the range~~ is from 20 to 150 microns.

25 Attempts were made to purify ~~the~~ ~~a~~ calcium ~~earbonate~~ ~~carbonate~~-rich by-product by ~~the~~ methods known in the prior art. Physical methods such as sieving, floatation, sedimentation and hydrocyclone separation were not successful, ~~which~~ The failure of prior art processes led to believe suggested that the impurities present in the calcium ~~earbonate~~ ~~carbonate~~-rich by-product are an integral part of the 30 material and not physically separate as in case of the conventional raw material, - limestone. Conventional chemical treatment methods were also found not suitable,

~~as because~~ the chemicals used were unable to leach the entrapped impurities from the calcium carbonate-rich by-product.

Therefore, it was decided to calcine the calcium ~~carbonate-carbonate-rich~~ by-product to obtain calcium oxide. When the calcium carbonate-rich by-product ~~it~~ was heated ~~at to~~ 900° C for one hour, the percent weight loss was 47.1% by weight and the X-Ray diffraction analysis indicated the presence of only calcium oxide. Therefore, it was inferred that some of the impurities can be removed by calcination of a calcium ~~carbonate-carbonate-rich~~ by-product, which by-product can be subjected to hydration and carbonation to obtain precipitated calcium carbonate.

Therefore, in the present invention, a process is developed for the production of precipitated calcium carbonate from a calcium ~~carbonate-carbonate-rich~~ by-product generated in industrial processes, specifically from a nitrophosphate fertilizer plant ~~is developed, which~~ The process comprises feeding continuously ~~the~~ a wet calcium ~~carbonate-carbonate-rich~~ by-product containing up to 25% moisture and having a particle size in the range of from 20 to 150 microns into a calciner maintained at above 850°C and below 950°C, at a feed rate ~~of from~~ 5 to 20 kg/h. The residence time of the material in the calciner is varied from 30 to 90 minutes by varying the rotation speed of the calciner from 0.5 to 2 RPM at an angle of inclination of 1.08 degrees. ~~Calciner~~ The calciner is provided with the ~~arrangements—means~~ to remove ~~the~~ liberated water vapors, carbon dioxide, ammonia and ~~NO_x-NO_x~~-containing exhaust gas into a scrubber, wherein ammonia and NO_x gases are scrubbed with water. The outlet rate of the calcined material varied from 2 to 10 kg/h. The calcined mass coming out is in a big lump form.

Therefore, ~~it~~ the calcined material is passed through a jaw crusher fitted ~~in between~~ the calciner and a material cooler. The crusher serves to crush the calcined material for crushing it into small lumps. The outlet material from the crusher is passed through ~~water-circulated jacketed~~ a screw conveyer type material cooler equipped with a circulating water jacket. The material cooler serves to for cooling the small lumps to near ambient temperature (from 40 to 50° C). Slaking of the calcined material obtained from the material cooler is carried out with water for one hour in a slaker provided with an agitator rotating which rotates at 120 RPM to

produce a hydrated lime slurry having a concentration from 15 to 23% by weight. Impurities present in the form of heavier and coarser particles were removed by sedimentation and / or by wet sieving through a 60 to 100 mesh sieve. The resulting slurry, from which the heavier/coarser particles have been removed, is

5 diluted to a desired concentration in the range from 10 to 20% by weight and then transferred into a carbonation reactor provided with the a sparger. Carbonation is accomplished by passing a carbon dioxide—air mixture containing 25% by volume carbon dioxide, at a gas velocity of from 10 to 15 cm/sec. and maintaining the temperature in the range from 25 to 45°C until the pH of the slurry falls to near

10 neutral, and separating. Then the precipitated material formed is separated by known methods. Drying and pulverizing. The separated solids are then dried and pulverized to get obtain precipitated calcium carbonate.

Optionally, the product slurry is was treated with fatty acid derivative an emulsion or solution of a fatty acid derivative at 95°C to get obtain from 2 to 3.5% by weight total fatty matter acid derivative in the a coated calcium carbonate. The

15 solids were recovered by known methods of filtration, drying and pulverizing to get obtain the coated calcium carbonate. The properties of Precipitated-precipitated calcium carbonate and coated Precipitated-precipitated calcium carbonate are given in Table 1, which. These properties indicated that it the products is would be

20 useful as filler in paints, plastics, rubber and PVC.

Table 1. Properties of Precipitated and Coated calcium carbonate.

Sr.No.	Properties	Precipitated	Coated
1	CaCO ₃ , (by Acidimetry), % weight, Min.	97	95
2	pH (5% slurry)	10-11	9.5-10.5
3	Total Nitrogen, % weight	Not traceable	Not traceable
4	Ammonical Nitrogen, % weight	Not traceable	Not traceable
5	Nitrate Nitrogen, % weight	Not traceable	Not traceable
6	Phosphate as P ₂ O ₅ , % weight	less than 1.0	less than 0.1
7	Mixed oxides, % weight	2.0-3.0	1.50-2.5
8	Fluoride as F ⁻ , % weight	0.04	0.02
9	Bulk density, tapped, g/mlmL	0.40-0.45	0.35-.40
10	Oil absorption, % weight	60-100	80-100
11	Whiteness / Brightness , %	96-98	97-99
12	Particle size, microns	less than 20	less than 20
13	Total Fatty Matter acid derivative, % weight	NIL	2.5-3.0

The percent available CaO in the calcined material was determined by the
Sugar method. ~~which~~ This method involved adding a known weight of the sample
in a 15% sugar solution and allowing ~~it~~ the sample to dissolve for 3 hours. ~~The~~
resulting solution was then ~~filtering the solution~~ filtered to remove ~~undissolved~~
5 undissolved solids. ~~and titrating a~~ An aliquot of the filtrate was then titrated with a
standardized acid.

The product properties were determined ~~as per the~~ by methods that are
described as follows.

The calcium carbonate content of the product ~~is~~ was determined by adding
10 an accurately weighed about 2 g of sample (approximately 2 g) in to a known
volume of standard acid. ~~allowing it~~ The sample was allowed to react completely.
~~and titrating the unused acid~~ The unreacted acid was then titrated with a
standardized alkali solution. Mixed oxides ~~are~~ were determined by precipitating
hydroxides from an acidic solution of the sample. ~~followed by ignition of~~ The
15 precipitated hydroxides were then ignited and weighing weighed as the
corresponding oxides. Phosphates ~~are~~ were determined by a spectrophotometric
method. Ammonical nitrogen, nitrate nitrogen and fluoride ~~are~~ were determined by
ion-selective electrodes. Tapped bulk density ~~is~~ was measured by noting the
volume of material after tapping ~~50 times of~~ a known weight of the sample 50
20 times in a calibrated cylinder. Whiteness/brightness ~~is~~ was measured by measuring
the reflectance of the sample and comparing with the reflectance of magnesium
carbonate (considered as 100% whiteness) and ~~with that the reflectance~~ of carbon
black (considered as zero percent whiteness). The particle size ~~is~~ was determined
using Mastersizer-2000 (Malvern, UK), particle size analyzer ~~as on the~~ dry powder.
25 The total content of fatty matter acid derivative in the coated precipitated calcium
carbonate is ~~was~~ determined by extracting the coated material with absolute
alcohol, separating the same and evaporating the solvent to ~~get~~ isolate the coating
material as a residue.

The process for the production of precipitated calcium carbonate according
30 to the present invention, uses a new kind of raw material which is a by-product
generated in a nitrophosphate fertilizer plant. This raw material has, hitherto not
been used for the this purpose. ~~This raw material having~~ has a particle size in the

range from 20 to 150 microns and ~~containing~~contains various types of impurities not usually found in the conventionally employed raw material, —limestone. Considering the scientific knowledge about the type of impurities present in a calcium carbonate ~~carbonate~~-rich by-product, it was possible to find out the data
5 for such a material with regard to its decomposition or sublimation temperature, ~~which~~This information is described below:

Moisture can be removed from the calcium carbonate-rich by-product by drying the material at 105-110°_C for a sufficient period. Ammonium carbonate decomposes at 58°_C, ~~ammonium~~ Ammonium bicarbonate decomposes between
10 36- and 60°_C and sublimes, ~~ammonium~~ Ammonium nitrate decomposes at 210° C, ~~ammonium~~ Ammonium chloride and ammonium fluoride ~~sublimate~~sublime at 335°_C.

Calcium nitrate (anhydrous) melts at 561°_C, ~~calcium~~ Calcium nitrate trihydrate melts at 51.5°_C, ~~calcium~~ Calcium nitrate tetrahydrate decomposes at
15 132°_C. Calcium mono- and di-phosphates decompose below 205°_C, whereas calcium tri- and pyro-phosphate melt above 1200°_C. Calcium hydroxide is converted to CaO and water between 580 and 600°_C.

~~Aragonite~~ Aragonite-type calcium carbonate decomposes at 825°_C, whereas calcite type calcium carbonate decomposes at about 895°_C, ~~into~~Both
20 aragonite and calcite decompose to form ~~Calcium~~ calcium oxide and ~~Carbon~~ carbon dioxide. If calcium carbonate is heated above 1000°_C, it forms dead burnt / inactive ~~Calcium~~ calcium oxide and liberates ~~Carbon~~ carbon dioxide. It ~~was~~is also known that active calcium oxide ~~could~~can be slaked to obtain hydrated lime which can be further carbonated to produce precipitated calcium carbonate.

25

The advantages involved in the claimed process include:

- Using a raw material without pre-drying or crushing.
- Keeping the material in ~~free~~ free-flowing conditions throughout the processing.
- 30 - Removal of the chemical impurities during calcination.
- Improving brightness without using any special reagent.

- Calcination of very fine (from 20 to 150 micron) and highly dense (bulk density 1.3 to 1.35 g/~~mm~~mL) particles with minimum dusting.
- Avoiding the requirement of special types of material ~~of~~ for construction of the calciner by limiting the calcination temperature to below 1000°_C temperature.
- Limiting the effect of calcination to removal of impurities without forming the dead burnt lime.
- ~~Arrangements~~ Means for scrubbing ~~the~~ liberated gases to avoid pollution of the surrounding environment.

The following examples are given by way of illustrations and therefore should not be construed to limit the scope of the present invention.

EXAMPLE -1

~~The~~ A calcium carbonate ~~carbonate-rich~~ by-product generated in a nitrophosphate fertilizer plant, having 12% moisture, was dried to a moisture content of <1% in a rotary dryer, ~~and~~ The dried calcium carbonate-rich by-product was fed at the rate of 10 kg/h into a rotary calciner. The rotary calciner was preheated to 875°_C with an angle of inclination 1.08 and a shell rotation speed of 1.5 RPM. The hold-up time was 35 minutes and the outlet rate was 5.2 kg/h. The product material was found to have 37% by wt. available CaO indicating incomplete calcination.

EXAMPLE -2

~~The~~ A calcium carbonate ~~carbonate-rich~~ by-product generated in a nitrophosphate fertilizer plant, having 12% moisture was dried to a moisture content of <1% in a rotary dryer. The dried calcium carbonate-rich by-product was ~~and~~ fed at the rate of 10 kg/h into a rotary calciner. The calciner was preheated to 875°C with an angle of inclination of 1.08 degrees and a shell rotation speed of 0.75 RPM. The ~~hold~~ hold-up time of the material in the calciner was 60 minutes and the outlet rate was 5.10 kg/h. The calcined mass obtained thereby was found to have 75% available CaO. The calcined material was crushed ~~after crushing to~~ into

small lumps. ~~The crushed calcined material is~~ was subjected to slaking for a period of one hour in a slaker so as to obtain a suspension having about 20% by weight solids. ~~It~~ The suspension was wet sieved through a 100 mesh sieve to remove grit particles. ~~The sieved material was and~~ diluted to obtain a slurry containing about 10% solids ~~slurry~~. This slurry ~~is~~ was subjected to carbonation by passing through the slurry a carbon dioxide-air mixture containing 25% by volume carbon dioxide at a superficial gas velocity of about 12.5 cm/sec, ~~and maintaining the~~ The temperature of the carbonation was maintained in the range from 25 to 45°C until the pH of the suspension ~~falls~~ dropped to near neutral. The carbonation was ~~accomplished~~ completed within about 90 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having~~ contained about 80% calcium carbonate, with a bulk density of about 0.50 g/mL ~~and an~~ average particle size of above 10 microns.

15

EXAMPLE-3

~~The~~ A calcium carbonate ~~carbonate-rich~~ by-product generated in a nitrophosphate fertilizer plant, having 12% moisture was dried to a moisture content of <1% in a rotary dryer. ~~The dried calcium carbonate-rich by-product was and~~ fed at the rate of 5 kg/h into a rotary calciner. The calciner was preheated to 950°C with an angle of inclination of 1.08 degrees and a shell rotation speed of 0.50 RPM. The ~~hold~~ hold-up time was 90 minutes and the outlet rate was 1.7 kg/h. The calcined mass obtained was found to have 88% available CaO. The calcined material ~~after crushing to~~ was crushed into small lumps. ~~The crushed calcined material is~~ was subjected to slaking for a period of one hour in a slaker so as to obtain a suspension having about 20% by weight solids. ~~It~~ The suspension was wet sieved through a 100 mesh sieve to remove grit particles and diluted to obtain a slurry containing about 10% solids ~~slurry~~. This slurry ~~is~~ was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 12.5 cm/sec. ~~and maintaining the~~ The temperature of the carbonation was maintained in the range from 25 to 45°C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90 minutes. Thereafter, the

product ~~is was~~ recovered by known methods. The product ~~was having~~contained about 98% calcium carbonate, with a bulk density of about 0.42 g/ml-mL and an average particle size in of about 6 microns with 100% of the particles having a particle size less then than 20 microns.

5

EXAMPLE-4

The ~~A~~ calcium carbonate ~~carbonate-rich~~ by-product generated in a nitrophosphate fertilizer plant, having 12% moisture was dried to a moisture content of <1% in a rotary dryer. The dried calcium carbonate-rich by-product
10 was~~and~~ fed at the rate of 10 kg/h into a rotary calciner. The calciner was preheated
to 950° C with an angle of inclination of 1.08 dcgrees and a shell rotation speed of 0.50 RPM. The hold-up time was 90 minutes and the outlet rate was 4.08 kg/h. The calcined mass obtained was found to have 88% available CaO. The calcined material was crushed into small lumps. ~~is~~ The crushed calcined material was
15 subjected to slaking ~~after crushing to small lumps~~ for a period of one hour in a slaker so as to obtain a suspension having about 20% by weight solids. ~~It~~ The suspension was wet sieved through a 100 mesh sieve to remove grit particles and then diluted to obtain a slurry containing about 10% solids-slurry. This slurry is was subjected to carbonation by passing a carbon dioxide-air mixture containing
20 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 12.5 cm/sec. ~~and maintaining the~~ The temperature of the carbonation was maintained in the range from 25 to 45° C; until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90 minutes. Thereafter, the product ~~is was~~ recovered by known methods. The product
25 ~~was having~~contained about 98% calcium carbonate, with a bulk density of about 0.42 g/ml-mL and an average particle size of about 6 microns with 100% of the particles having a particle size of less then 20 microns.

EXAMPLE-5

30 The ~~A~~ calcium carbonate ~~carbonate-rich~~ by-product generated in nitrophosphate fertilizer plant, having 23% moisture was dried to a moisture content of <1% in a rotary dryer. The dried calcium carbonate-rich by-product

was ~~and~~ fed at the rate of 10 kg/h into a rotary calciner. The calciner was preheated to 950° C with an angle of inclination of 1.08 degrees and a shell rotation speed of 0.50 RPM. The ~~hold~~ hold-up time was 90 minutes and the outlet rate was 4.18 kg/hr. The calcined mass obtained was found to have 88% available CaO. The
5 calcined material was crushed into small lumps. The crushed calcined is material ~~was~~ subjected to slaking ~~after crushing to small lumps~~ for a period of one hour in a slaker so as to obtain a suspension having about 20% by weight solids. ~~It~~ The suspension was wet sieved through a 100 mesh sieve to remove grit particles and then diluted to obtain a slurry containing about 10% solids ~~slurry~~. This slurry is
10 was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 12.5 cm/sec. and ~~maintaining the~~ The temperature of the carbonation was maintained in the range from 25 to 45° C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90
15 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having contained~~ about 98% calcium carbonate, with a bulk density of about 0.42 g/ml ~~mL~~ and an average particle size of about 6 microns with ~~100% particles a~~ maximum particle size of less than 20 microns.

20

EXAMPLE-6

Pre-dried calcium ~~carbonate~~ carbonate-rich by-product having a particle size in the range from 20 to 150 microns and a moisture content of <1%, was introduced into a Fluidized Bed Calciner at the rate of 10 kg/h. A fluidized bed was formed by passing hot air through the calciner tower at a lower gas velocity of
25 about 100 cm/sec. The temperature of calcination was maintained at around 950° C by injecting fuel at a controlled rate. Within 60 minutes the desired calcined mass having 88 % available CaO ~~is~~ was obtained at the outlet rate of 5.7 kg/h. The calcined material ~~is~~ was subjected to slaking for a period of one hour in a slaker so as to obtain a suspension having about 20% by weight solids. ~~It~~ The suspension
30 was wet sieved through a 100 mesh sieve to remove grit particles and diluted to obtain a slurry containing about 10% solids ~~slurry~~. This slurry is subjected to carbonation by passing through the slurry a carbon dioxide-air mixture containing

25% by volume carbon dioxide at a superficial gas velocity of about 12.5 cm/sec. ~~and maintaining the~~ The temperature was maintained in the range from 25 to 45° C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having contained~~ about 98% calcium carbonate, with a bulk density of about 0.42 g/ml and an average particle size of about 6 microns with ~~100% particles~~ a maximum particle size of less than 20 microns.

EXAMPLE-7

~~The~~ A by-product calcium carbonate with 1% moisture was calcined at 950° C in a rotary calciner for 90 minutes to obtain 88% active calcium oxide. The calcined material ~~which~~ was crushed to small lumps using a jaw crusher and cooled to below 50° C using a water circulated jacketed screw ~~conveyer~~ conveyer-type material cooler. ~~7~~ Seven kg. of this material was added to 35 liters of water ~~kept~~ in a 50 liters capacity slaker. The slaker was provided with a paddle type agitator which was operated at a maximum speed of 120 RPM to obtain a 20% weight by volume slurry. The reaction was found to be exothermic with a maximum rise in temperature of about 40° C. The slurry was continuously agitated for one hour so as to achieve complete conversion of calcium oxide to calcium hydroxide. This slurry ~~is~~ was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 12.5 cm/sec. ~~and maintaining t~~ The temperature of the carbonation was maintained in the range from 25 to 45° C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having contained~~ about 98% calcium carbonate, with a bulk density of about 0.42 g/ml ~~mL~~ and an average particle size of about 6 microns with ~~100% particles~~ a maximum particle size of less than 20 microns.

EXAMPLE-8

The ~~A~~ by-product calcium carbonate with 1% moisture was calcined at 950° C in a rotary calciner for 90 minutes to obtain 88% active calcium oxide. The calcined material ~~which~~ was crushed to small lumps using a jaw crusher and cooled to below 50° C using a water circulated jacketed screw conveyor-conveyer-type material cooler. ~~It~~ The crushed calcined material was further pulverized to -150 mesh powder. The pulverized material (7 kg) ~~of this material~~ was added to 35 liters of water ~~kept~~ in a 50 liters capacity slaker, provided with a paddle type agitator. The slaker was operated at a maximum speed of 120 RPM to obtain a slurry containing 20% weight by volume slurry. The slurry was continuously agitated for one hour so as to achieve complete conversion of calcium oxide to calcium hydroxide. The reaction was found to be exothermic with maximum rise in temperature of about 40° C. This slurry ~~is~~ was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide ~~through the slurry~~ at a superficial gas velocity of about 12.5 cm/sec. ~~and maintaining~~ The temperature of the carbonation was maintained in the range from 25 to 45° C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 90 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having~~ contained about 98% calcium carbonate, with a bulk density of about 0.42 g/mL and an average particle size of about 6 microns with 100% particles and a maximum particle size of less than 20 microns. This indicated that there was no advantage in using a powdered calcined mass as compared to using a calcined mass crushed into small lumps in the slaking process.

25

EXAMPLE-9

Seventy liters of ~~the~~ a slaked lime slurry having about 20% solids, was prepared under ~~similar~~ conditions as similar to those described in Example-7. The slurry is ~~was~~ transferred to a jacketed carbonation reactor consisting of a bubble column provided with a ~~specially designed~~ sparger specially designed to create sufficient turbulence for continuous mixing within the column. The reactor was further provided with arrangements for monitoring the reaction temperature and

30

the pH and cooling/heating arrangements using the jacket provided. The carbonation was accomplished-completed within 90 minutes by passing mixture of air and a CO_2 -air mixture containing 25 volume % CO_2 at a superficial gas velocity of about 12.5 cm/sec. The carbonation temperature was maintained and maintaining the temperature in the range from 25 to 45° C, wherein the mixed gas contained 25% by volume CO_2 and remainder being air. Sufficient-A sufficient amount of the gas mixture was passed through the slurry to bring the pH of the slurry to neutral. When no further increase in pH (more than 7) was observed, the carbonation was stopped. Thereafter, The precipitated calcium carbonate formed in the carbonation was isolated by filtration, followed by washing, drying and pulverizing. The product has-contained about 98% calcium carbonate purity, with a bulk density in the range from 0.40-0.45 g/mL-and, an average particle size of about 6 microns and a maximum particle size of with 100% particles below-less than 20 microns.

15

EXAMPLE-10

The-A slurry of precipitated calcium carbonate obtained as per-described in Example-7, was heated to 95° C under-with continuous agitation. To this slurry was added; an emulsion of a fatty acid derivative such as stearic acid with caustic soda, was-added-in an amount of 3.5% by weight of the calcium carbonate to be produced. The slurry was allowed to cool to 40-45° C under-with stirring to get obtain a coated product. The coated product, which-iswas isolated by filtration, followed by washing, drying and pulverizing. The properties of this coated precipitated calcium carbonate is-are as-givenprovided in Table 1.

25

EXAMPLE-11

The-A slurry of precipitated calcium carbonate obtained as per-described in Example-7, was heated to 95° C under-with continuous agitation. To this slurry was added; an emulsion of a fatty acid derivative such as stearic acid with caustic soda, was-added-in an amount of 2.0% by weight of the calcium carbonate to be produced. The resulting slurry was allowed to cool to 40-45° C under-with stirring to get-obtain a coated product,-. The coated productwhich-is was isolated by

30

filtration, followed by washing, drying and pulverizing. The total content of ~~total~~ fatty ~~matter~~ acid derivative in the coated product was 1.6% by weight. Other properties of the product were similar to those ~~given~~ provided in Table 1.

5

EXAMPLE-12

The ~~A~~ by-product calcium carbonate with 1% moisture was calcined at 950°_C in a rotary calciner for 90 minutes to obtain 88% active calcium oxide. The calcined material ~~which~~ was crushed to small lumps using a jaw crusher and cooled to below 50°_C using water circulated jacketed screw ~~conveyer~~ conveyer-type material cooler. 7-Seven kg. of ~~this~~ the crushed material was added to 35 liters of water kept in a 50 liters capacity slaker~~,-~~. The slaker was provided with a paddle type agitator. The slaker was operated at maximum speed of 120 RPM to obtain a 20% weight by volume slurry. The reaction was found to be exothermic with maximum rise in temperature of about 40°_C. The slurry was continuously agitated for one hour so as to achieve complete conversion of calcium oxide to calcium hydroxide. This slurry ~~is~~ was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 15.0 cm/sec. ~~and maintaining the~~ The carbonation temperature ~~was maintained~~ in the range from 25 to 45°_C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 75 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having~~ contained about 97% calcium carbonate, with a bulk density of about 0.45 g/~~ml~~ mL, and average particle size of about 7 microns and a maximum particle size of ~~with 100% particles~~ less than 25 microns.

25

EXAMPLE-13

The ~~A~~ by-product calcium carbonate with 1% moisture was calcined at 950°_C in a rotary calciner for 90 minutes to obtain 88% active calcium oxide. The calcined material ~~which~~ was crushed to small lumps using a jaw crusher. The crushed material ~~and~~ was cooled to below 50°_C using a water circulated jacketed screw ~~conveyer~~ conveyer-type material cooler. 7-Seven kg. of ~~this~~ the crushed material was added to 35 liters of water kept in a 50 liters capacity slaker~~,-~~. The

30

5 slaker was provided with a paddle type agitator. The slaker was operated at a maximum speed of 120 RPM to obtain a 20% weight by volume slurry. The reaction was found to be exothermic with maximum rise in temperature of about 40°_C. The slurry was continuously agitated for one hour so as to achieve maximum conversion of calcium oxide to calcium hydroxide. ~~This~~ The resulting slurry ~~is~~ was subjected to carbonation by passing a carbon dioxide-air mixture containing 25% by volume carbon dioxide through the slurry at a superficial gas velocity of about 10.0 cm/sec. ~~and maintaining~~ The carbonation temperature was maintained in the range from 25 to 45°_C, until the pH of the suspension ~~fallen~~ dropped to neutral. The carbonation was ~~accomplished~~ completed within 140 minutes. Thereafter, the product ~~is~~ was recovered by known methods. The product ~~was having~~ contained about 97% calcium carbonate, with a bulk density of about 0.45 g/ml, and average particle size of about 7 microns and a maximum particle size of ~~with 100% particles~~ less than 25 microns.

15

EXAMPLE-14

The ~~A~~ slaked lime slurry was obtained as described in Example-7. The slaked lime slurry was diluted to 10% wt/vol. of CaO and taken in a continuous stirred tank reactor equipped with an agitator, having height/diameter ratio of about 2. ~~Keeping~~ The slurry was kept continuously agitated at 100 RPM, ~~a~~ A mixture of CO₂ and air in ~~the~~ a ratio of ~~30 to 70~~ 30 to 70 and a space velocity of 2 cm/sec was introduced at ambient temperature. The reaction pH was found to come to neutral towards the completion of carbonation within 50 minutes. ~~On stopping~~ When the gas flow was stopped the pH ~~was increasing~~ continued to rise up to 8.0. The carbonation was continued for further 10 minutes to ~~get~~ obtain a steady pH of 7.0 ~~for further 10 minutes~~. ~~The~~ A solid product was isolated, dried and pulverized to ~~get~~ obtain a precipitated calcium carbonate and a coated product as described in Example-10. The properties of the coated precipitated calcium carbonate thus obtained ~~was~~ were the same as ~~given~~ the properties provided in Table 1.

30

~~The a~~Advantages of the present invention are include

1. Calcium ~~earbonate~~carbonate-rich by-product generated in industrial processes, specifically in nitrophosphate fertilizer plants, is converted to precipitated calcium carbonate by calcination, slaking and carbonation using conventionally used machinery.
2. ~~A C~~A calcium ~~earbonate~~carbonate-rich by-product is converted to ~~value~~value-added material suitable for applications in rubber, paint, PVC and plastics manufacture.
3. An alternative source to limestone is provided for producing precipitated calcium carbonate useful for commercial applications ~~is found out~~is disclosed.
4. ~~A C~~A calcium ~~earbonate~~carbonate-rich by-product having a fine particle size from 20 to 150 microns is successfully treated without contributing to pollution, due to dusting, which is commonly associated with such fine powders ~~due to dusting~~.
5. A continuous process ~~has been developed~~is provided according to the present invention, which can be linked ~~with~~to the plant generating the calcium ~~earbonate~~carbonate-rich by-product. ~~Thus,~~This linked process can minimized the solid waste pollution caused by such by-products and improved the environmental quality of a nitrophosphate fertilizer plant.
6. ~~As~~Because the temperature of calcination of ~~the a~~a calcium ~~earbonate~~carbonate-rich by-product is around 950°C, special types of ~~material of~~ construction materials ~~is are~~ not required to be used in the calciner.
7. Calcination according to the present invention provides the special advantage of removing all the major impurities simultaneously and converting the calcium ~~earbonate~~carbonate-rich by-product to active calcium oxide. Therefore, ~~not many~~few unit operations are required in claimed purification process.

PROCESS FOR GENERATION OF PRECIPITATED CALCIUM
CARBONATE FROM CALCIUM CARBONATE
RICH INDUSTRIAL BY-PRODUCT

ABSTRACT OF THE INVENTION

An environmentally friendly process for the production of precipitated calcium carbonate suitable for industrial application from a calcium carbonate-carbonate-rich by-product of a nitrophosphate fertilizer plant. ~~by adopting~~ The process
employs purification steps of calcination, carbonation and optional treatment with
an emulsion of fatty acid or its fatty acid derivatives.